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PHYSICAL METHODS OF INVESTIGATION

Physicochemical Investigation of Anodic Processes Involved in Silver Electrowinning in Refining Technology

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Abstract—During silver electrowinning in refining technology, irrespectively of the nature of electrolyte and anode material, an anode deposit is formed due to oxidation of singly charged silver ions to higher degrees of oxidation (+2 and +3) under polarization. Absorption spectra of Ag(II) have been obtained in solutions with various concentrations of silver ions and nitric acid using anodic polarization in combination with electronic absorption spectroscopy; silver ions of high oxidation degrees were found to be unstable in solutions. At anode potentials $\varphi_a \geq 1.15–1.22$ V, Ag(I) ions in liquid phase are oxidized to Ag(II), which paint the anolyte; their content depends on silver and nitric acid concentrations in the electrolyte. The deposit crystallizes on anode at potential $\varphi_a \approx 1.5$ V. Chemical analysis, X-ray powder diffraction, and a thermogravimetric study of the anode deposit have made it possible to identify its initial composition as $Ag_7O_8NO_3$. The deposit composition varies in time as a result of reduction of highly oxidized silver.

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In large-scale refining technology, an important position is occupied by silver electrowinning using insoluble anodes to produce cathode deposits [1, 2]. During silver electrowinning from nitric acid solutions, dark grey needlelike substances are deposited onto the surface of platinized titanium anodes (PTAs); their formation is accompanied by a change of electrolyte color. It is required to study the chemistry of the process and to ascertain the ability of Ag^+ ions to oxidize on the surface of the insoluble anode to form a deposit.

Formation of dark grey crystals on anodes in electrolytes of various compositions (NO_3^-, SO_4^{2-}, F^-, ClO_4^-) is typical both for electrorefining and for electrowinning [3–5].

When an anode deposit is formed, silver can oxidize to valences higher than Ag(I) [6, 7], which was confirmed by a spectral method [8].

The values of Ag^I/Ag^{II} potentials were determined to be 1.59, 1.74–1.77 V [9] and 1.93–2.0 V [10]. An accurate determination of the Ag^I/Ag^{III} normal potential is impossible because of the instability of Ag^{III} in the form of AgO^+, when trivalent ions are reduced to Ag(II) in the presence of monovalent silver [11, 12].

The deposits formed on anode were identified as $Ag_7O_8NO_3$, $Ag^{II}O$, $Ag^IAg^{III}O_2$, and Ag_2O_3 [3]. For a nitric acid medium, the following formula has been proposed: $Ag_5^{3+}Ag_2^+O_8NO_3$. The existence of Ag_4O_5 oxide is refused [13]. Microscopic examination of deposits demonstrated that in nitrate and fluoride solutions deposits were crystallized in the form of octahedrons, and in perchlorate solutions, in the form of cubes. The deposits obtained from nitrate electrolytes contained 79.9 wt % silver according to the formula $2Ag_3O_4 \cdot AgNO_3$ [14]. A structural study of deposits showed the following content of silver atoms in a cell: 4 Ag(I) and 24 Ag(II). The following general formula of the compound is proposed: $4AgO \cdot 2AgO_2 \cdot AgNO_3$, or $Ag^IAg_6^{III}O_4(O_2)NO_3$.

Analysis of the higher oxide states of silver makes it possible to assume that divalent silver oxide AgO can be presented in the form of $Ag^I–Ag^{III}$, and compound Ag_7NO_{11} , in the form of $Ag(Ag_3O_4)_2NO_3$ [15].

EXPERIMENTAL

Formation of anode deposits during silver electrowinning from nitric acid and sulfuric acid electrolytes was studied using a laboratory bench equipped with a YaSE-2 electrochemical cell, 0.7 L in volume, with anode and two titanium cathodes (Vt1-0).

In obtaining anode polarization curves, an anode made of gold (grade ZlA-1P) was used in order to exclude the influence overvoltage.

Model electrolytes with composition of (g/L) 170–180 Ag and 1.5–2 HNO_3 (H_2SO_4), produced by dissolution of crystalline silver (grade SrA-1) in nitric and sulfuric acids (high purity grade) were typically close to commercial samples in terms of the contents of metal and free acid. In order to eliminate problems in diffusion during electrowinning, the electrolyte was agitated using a magnetic stirrer. The electrolyte tem-

Parameters of anode deposit formation

Anode	Electrolyte composition, g/L		Anode current density, A/m^2	Variations of anode potential, V	Electrolyte temperature, K	Formation of anode deposit, min
	Ag	HNO_3				
Ti-Mn	160	≤2	425–1400	1.7–3.8	293–335	5–10
OR-TA	181		480–900	1.8–2.0	296–339	15
PTA (platinized titanium anodes)	180		430–1000	1.7–1.9	297–313	4–10

perature in the cell was maintained constant using a thermostat.

The electric circuit consisted of a TE1-100/12T-OUKhL4 rectifier, a PI-50-1.1 potentiostat, a PR-8 programming unit, a PDA-1 two-dimensional recording device, and M-2051 and M-2044 voltammeters used as an ammeter and a voltmeter, respectively. Anode potentials were determined using a circuit composed of an Ag/AgCl reference electrode and intermediate reservoirs with saturated KNO_3 and KCl solutions in order to exclude AgCl formation in the electrolyte and distortion of measurements.

Anode polarization curves were recorded in a dynamic mode with a scan rate of 200–800 mV/s, which excluded fluctuations in solution concentrations and decelerated formation of an anode deposit, thus increasing the accuracy of calculation of current density. Measurements were carried out in three replica experiments. After the experiment was over, for the purpose of subsequent atomic emission analysis, the deposit was removed from the anode surface, which was then washed with concentrated nitric acid; the titanium cathode was cleaned from a silver deposit; and then the electrodes were washed with distilled water and dried with paper filter.

Electronic absorption spectra (EAS) were recorded for the initial electrolytes and after dissolution of anode deposits on a UNICO-1200 spectrophotometer in the wavelength range of 300–1200 nm in 10-mm pyrex cells.

Oxidation of silver during electrowinning, accompanied with a variation in optical density of solutions, was studied using a combined electrochemical spectral unit, which facilitated recording EASs of the electrolyte in a potentiostatic mode at fixed values of the anode potential φ_a. The optical density of solution $D \geq 0.1$ was used as a criterion of the existence of oxidized silver ions.

The phase analysis of anode deposit samples was performed using an XRD 7000 SHIMADZU diffractometer (CuK_α radiation, graphite monochromator). Thermogravimetric and calorimetric analysis was carried out using a NETZSCH STA 449C Jupiter derivatograph.

The composition of the evolved gaseous phase was determined using a QMS 403C Aëolos quadrupole mass spectrometer coupled with a thermal analyzer.

Samples in alumina crucibles were heated to 873 K at a constant rate of 10 K/min in an argon flow (30 mL/min) and in air (50 mL/min) to be subsequently used in differential scanning calorimetry (DSC) and differential thermal analysis (DTA), respectively. Sample weights were 30 mg (DSC) and 70 mg (DTA).

RESULTS AND DISCUSSION

It was established that formation of an anode deposit during silver electrowinning is not influenced by the nature ($AgNO_3$, Ag_2SO_4) and concentration of the electrolyte (50–170 g/L), nor by the composition of the insoluble anode: formation of a solid phase at a cell voltage of ~2 V and an anode current density of 310–420 A/m^2 in 2–3 min from the current input is preceded by a change in electrolyte color, which is stipulated by the occurrence of highly oxidized silver in the liquid phase.

Fine dark grey crystals precipitated on the anode surface, acquiring with time a needle-like configuration oriented to the cathode. With an increase in size the deposit needles were broken and, falling to cell bottom, slowly dissolved with gas evolution. When disconnecting the current load, the deposit of the anode surface also dissolved in nitric acid electrolyte, changing its color.

During electrowinning it has been found that when the nitric acid content exceeded 70 g/L, the anode deposit was not formed; intensive gas evolution occurred on the anode.

Therefore, formation of anode deposits during electrowinning is determined by concentration of free acid in electrolyte, provided that anode polarization is imposed.

An anode deposit, obtained in commercial cells, contained, wt %: 79.8 Ag, 0.0034 Au, 0.003 Pd, and <0.005 Pt; in terms of the silver content the deposit corresponds to the formula: Ag_7NO_{11} with a probability of 99.9 %.

In order to interpret the polarization curves of silver electrowinning and to account for the influence of

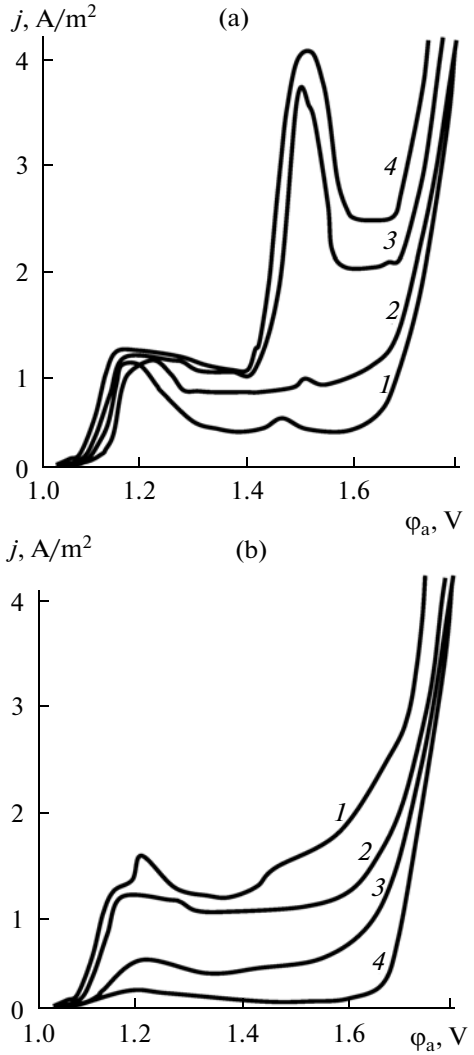

Fig. 1. Current density as a function of anode potential for electrolyte compositions, g/dm^3: (a) 50 Ag and (b) 150 Ag; (*1*) 20 HNO_3, (*2*) 30 HNO_3, (*3*) 40 HNO_3, and (*4*) 60 HNO_3.

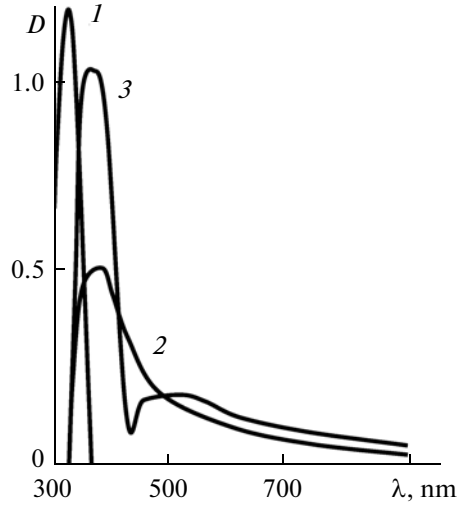

Fig. 2. Optical density of silver solutions as a function of wavelength: (*1*) Ag(I) and (*2*, *3*) Ag(II).

NO_3^- anion on the anodic process, we first determined the influence of anode potential (φ_a, V) on current density (j, A/m^2) in silver-free solutions of 20–60 g/L HNO_3. At φ_a = 1.4–2 V electrode polarization occurs and current density is close to zero. In the range of φ_a = 2–2.35 V, the current density increases to j = 2400 A/m^2, oxygen is evolved, and no deposit is formed on the anode. With an increase in nitric acid concentration, the oxygen overvoltage increases from 0.5 to 0.6 V.

At sufficiently moderate current densities ($j \le 4$ A/m^2) and silver concentrations (Ag ≤ 50 g/dm^3) in the electrolyte (20–60 g/L HNO_3), the polarograms plotted in the coordinates j–φ_a, feature two peaks (at 1.15–1.22 and 1.45–1.48 V), as well as areas where the current density decreases (1.22–1.40 and 1.48–1.62 V) and is constant (1.40–1.65 and 1.62–1.68 V) (Fig. 1a). The height of the second peak at φ_a = 1.45–1.48 V decreases as the nitric acid concentration decreases from 60 to 20 g/L.

With an increase in silver concentration in the electrolyte to 150 g/L, the first peak of increasing current density exists at the same potential values (1.15–1.22 V), and the second peak at φ_a = 1.45–1.48 V is nearly absent (Fig. 1b). The heights of the peaks decrease with an increase in ionic force of solution .

The existence of peaks in polarograms evidences successive oxidation of silver Ag^I–Ag^{II} in the electrolyte and crystallization of a deposit from Ag(II) solution, and the areas of constant current density, probably, correspond to the accumulation of oxidized metal species near the anode. With an increase in initial silver concentration to 150 g/L and when the amount of monovalent silver that provides the stability of Ag(III) is exceeded, further oxidation of silver to Ag(III) stops and the second peak at φ_a = 1.45–1.48 V is smoothened.

Since Ag(III) is unstable in Ag(I) solutions, as the monovalent silver concentration in the electrolyte increases, it is necessary to increase the duration of anode polarization in order for deposition to be quantitative.

In the region of high current densities j = 100–2000 A/m^2, a deposit and oxygen are evolved simultaneously on the anode. Initial oxidation of silver and accumulation of the oxidized species, detected at low current densities, occur at high rates at high current densities and are accompanied with a change in anolyte color followed by formation of a solid phase of oxidized compounds. Since the deposit on the anode grows rapidly and passivates its surface, no dependence on the electrolyte acidity can be found.

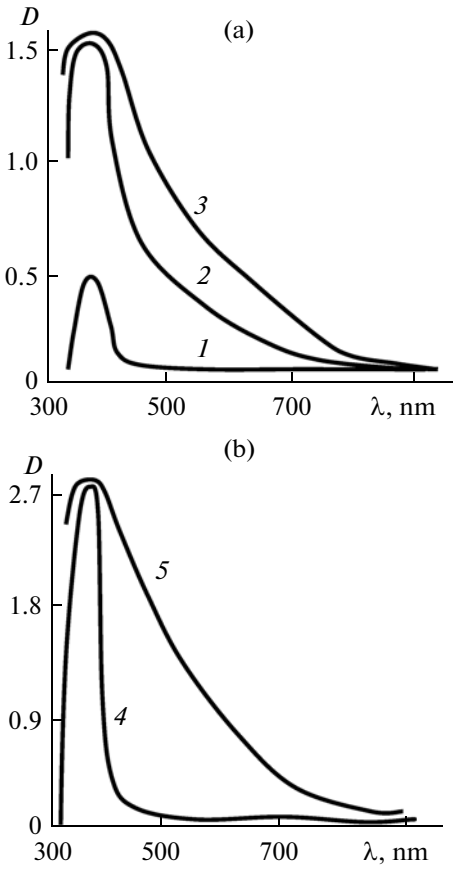

Fig. 3. Optical density of solutions with compositions, g/L: (a) 75 and (b) 150 Ag; (a) 50 and (b) 100 HNO_3 as a function of wavelength at potentials, V: (*1*) 1.5, (*2*) 1.6, (*3, 4*) 1.8, and (*5*) 1.9.

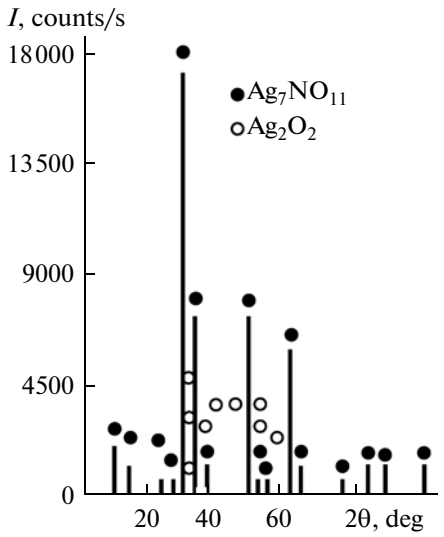

Fig. 4. Diffraction pattern of the anode deposit.

In order to identify the silver species existing in the anode deposit, we recorded its EAS spectra (Fig. 2) of initial electrolytes (curve *1*), of bivalent silver model systems obtained by addition of ammonium persulfate $(NH_4)_2S_2O_8$ to a nitric acid solution of $AgNO_3$ followed by dissolution of the newly formed deposit in HNO_3 (curve *2*), and nitric acid leaching solutions of commercial anode deposits (curve *3*).

The spectrum of monovalent silver consists of the long-wavelength edge of an intense absorption band, which starts at 320 nm, and has no other absorption bands in the range of 370–1200 nm.

The spectrum of bivalent silver model solutions has a peak at the boundary between the ultraviolet and visible regions of absorbed radiation at ~385 nm, displaced with time to 370 nm, which corresponds to λ = 350–500 nm [15].

The spectrum of the solution obtained by dissolution of a commercial anode deposit sample features a peak with the maximum optical density $D = 1$ in the range of 380–400 nm, which confirms the existence of highly oxidized silver in the anode deposit composition.

A study of silver oxidation during electrowinning from electrolyte with the composition 75 g/L Ag + 50 g/L HNO_3 demonstrated that, proceeding from polarization curves (Fig. 1), at anode potentials $\varphi_a < 1.5$ V the concentration of highly oxidized ions is so low that the electrolyte is virtually not colored (Fig. 3, curve *1*).

Coloration of the solution in the anode region, stipulated by quantitative appearance of Ag(II), was observed at $\varphi_a \geq 1.6$–1.9 V with the maximum optical density $D = 1.5$–2.7 in the range of $\lambda = 350$–380 nm (Fig. 3a) and at $\lambda = 400$ nm (Fig. 3b).

According to X-ray powder diffraction analysis (Fig. 4), the anode deposit contains the following silver compounds: oxynitrate $Ag(NO_3)(Ag_6O_8)$ (ICDD 01-071-0904) and oxide Ag_2O_2 (ICDD 00-051-0945) in a negligible amount (as a consequence of the low stability of silver oxynitrate).

Thermogravimetric studies of the anode deposit in an argon environment showed a stepwise decrease in sample weight (TG), %: 8.3 (95–180°C), 3 (180–380°C), and 8.7 (380–455°C) (Fig. 5a). The DTG curve features four minima at 124, 134, 158, and 450°C. The DSC curve, synchronously to a decrease in sample weight, features one exotherm (134°C) and two endotherms (207 and 452°C).

Analysis of the evolved gases showed a significant amount of oxygen with a strong mass variation with peak ionic currents (atomic mass unit 32) at 137 and 451°C (Fig. 5b). When samples are heated to temperatures higher than 250°C, the level of the ionic current (atomic mass unit 30 and 46) typical for nitrogen oxides NOO and NO_2 increases, with a maximum at 439°C.

The main component of the anode deposit, namely $Ag(NO_3)(Ag_6O_8)$ [16], is decomposed in the temperature range of 95–290°C with evolution of oxygen and formation of AgO and $AgNO_3$. The endotherm at

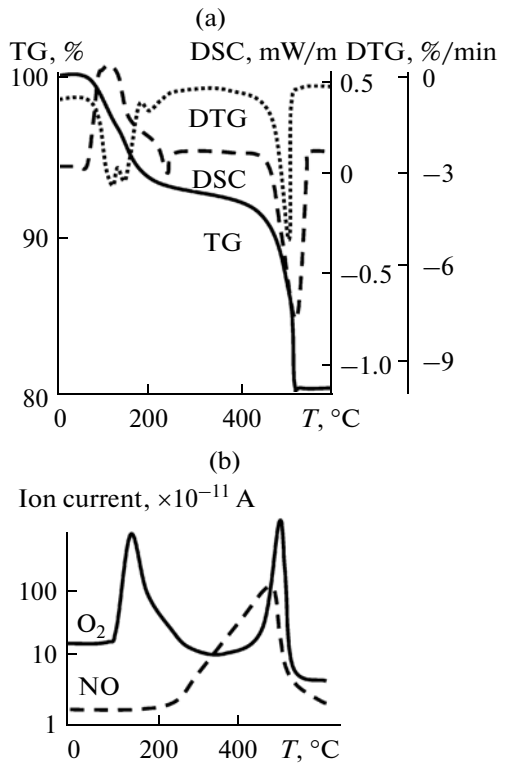

Fig. 5. Thermoanalytical curve of anode deposit (a) and mass-spectrograms of the gas phase (b).

207°C is probably due to melting of the $AgNO_3$ phase with formation of silver monoxide and oxygen in the temperature range of 250–500°C and further decomposition of AgO into the initial constituents.

The obtained experimental data do not contradict with a known scheme of temperature transformations of silver compounds in anode deposits [15]:

$$Ag_5^{3+}Ag_2^{+}O_8NO_3$$
$$\xrightarrow{\approx 120^\circ C(-O)} Ag_4^{3+}Ag_3^{+}O_7NO_3$$
$$\xrightarrow{\approx 130^\circ C(-O)} Ag_3^{3+}Ag_4^{+}O_6NO_3$$
$$\xrightarrow{\approx 153^\circ C(-O_2)} Ag^{3+}Ag_6^{+}O_4NO_3$$
$$\xrightarrow{\approx 180^\circ C(-O)} Ag_7^{+}O_3NO_3 \xrightarrow{\approx 438^\circ C(-3O_2-N)} 7Ag.$$

Therefore, during silver electrowinning in refining technology, an anode deposit is formed, irrespectively of nature of electrolyte and anode material, due to oxidation of singly charged silver ions to higher degrees of oxidation (+2 and +3) under polarization and achievement of the threshold Ag(II) and Ag(III) concentrations.

Based on the obtained polarization curves, the Ag^{I}–Ag^{II} valence transitions have been found and the crystallization of deposits from Ag(II) solution during the anode oxidation of $AgNO_3$ (φ_a = 1.15–1.22 and 1.45–1.48 V) in model solutions, which do not have quantitative character.

Using the combined methods of anode polarization and EAS, absorption spectra of Ag(II) have been obtained in solutions with various silver ions concentrations and color densities; silver ions of higher degrees of oxidation in solutions have been found to be unstable. At anode potentials $\varphi_a \geq 1.15$–1.22 V, Ag(I) ions in the electrolyte are oxidized to Ag(II) ions; their concentration and the color density of the anolyte depend on silver and nitric acid concentrations in the electrolyte. Crystallization of the anode deposit occurs ar $\varphi_a \approx 1.5$ V due to the appearance of Ag(III) ions.

Chemical analysis, X-ray powder diffraction, and a thermogravimetric study of the anode deposit have made it possible to identify its initial composition as $Ag_7O_8NO_3$. The initial composition of the deposit varies in time as a consequence of reduction of highly oxidized silver.

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